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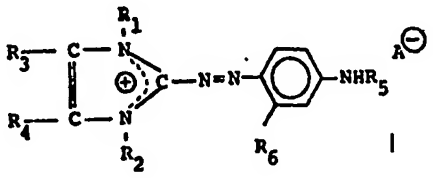
(54) **Improvements in or relating to organic compounds**

(57) Compounds of formula I



in which R_1 and R_2 are independently unsubstituted C_{1-4} alkyl,

R_3 and R_4 are independently hydrogen or unsubstituted C_{1-4} alkyl,

R_5 is hydrogen, unsubstituted C_{1-4} alkyl or C_{2-4} alkyl mono-substituted by OH or C_{1-4} alkoxy,

R_6 is halogen and

$A^{\ominus}$ is an anion,

are useful as basic azo dyestuffs having good fastness and migration properties.

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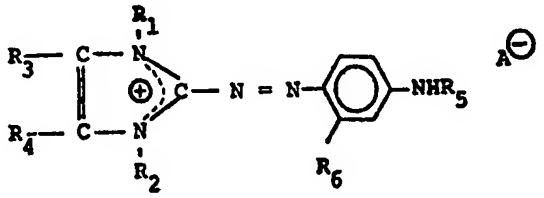
SPECIFICATION

Improvements in or relating to organic compounds

This invention relates to basic azo compounds free from sulphonic acid groups.

More particularly, the invention provides basic azo compounds of formula I



I

in which R_1 and R_2 are independently unsubstituted C_{1-4}alkyl,

R_3 and R_4 are independently hydrogen or unsubstituted C_{1-4}alkyl,

R_5 is hydrogen, unsubstituted C_{1-4}alkyl or C_{2-4}alkyl mono-substituted by OH or C_{1-4}alkoxy,

R_6 is halogen and

$A^{\ominus}$ is an anoin.

By 'halogen' is meant fluorine, chlorine or bromine.

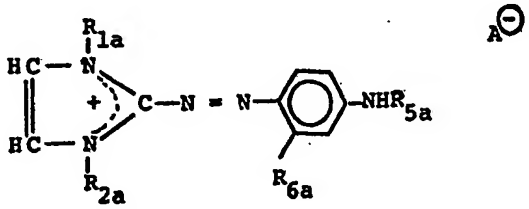
R_1 and R_2 are preferably R_{1a} and R_{2a}, where R_{1a} and R_{2a} are independently methyl or ethyl, more preferably R_1 and R_2 are both methyl.

R_3 and R_4 are preferably both hydrogen.

Where R_5 is unsubstituted alkyl it is preferably methyl or ethyl, more preferably methyl; where R_5 is substituted alkyl it is preferably 2-hydroxyethyl, 2-hydroxypropyl or 3-methoxypropyl. R_5 is preferably R_{5a} where R_{5a} is hydrogen, methyl, ethyl, 2-hydroxyethyl, 2-hydroxypropyl or 3-methoxypropyl; more preferably R_{5b} where R_{5b} is hydrogen or methyl.

R_6 is preferably R_{6a} where R_{6a} is fluorine or chlorine, more preferably chlorine.

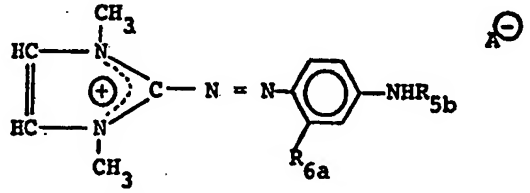
Preferred compounds of formula I are those of formula Ia



Ia

in which R_{1a}, R_{2a}, R_{5a}, R_{6a} and $A^{\ominus}$ are as defined above.

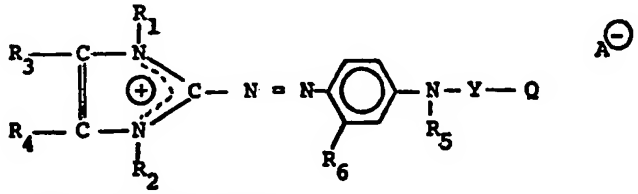
More preferred compounds are those of formula Ib



Ib

in which R_{5b}, R_{6a} and $A^{\ominus}$ are as defined above.

The invention also provides a process for the preparation of compounds of formula I, characterised by either a) treating a compound of formula II



II

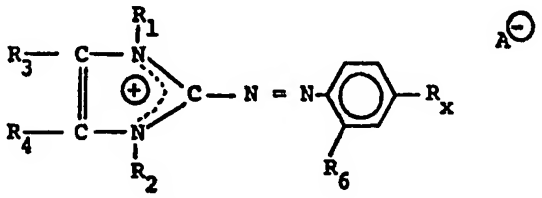
in which R_{1-6} and $A^{\ominus}$ are as defined above,

Y is —CO— or —SO_2—

and Q is C_{1-4} alkyl

with an acid HA in which A is a group capable of forming the anion $A^{\ominus}$, or

b) by reacting a compound of formula III



III

in which R_1, R_2, R_3, R_4 R_6 and $A^{\ominus}$ are as defined above and R_x is an anionic leaving group, for example halogen (including iodine) or alkoxy, whith a compound of formula IV

$$R_5\text{——}NH_2 \qquad \text{IV}$$

in which R_5 is as defined above.

The cleavage of the group —Y—O from compounds of formula II is suitably carried out in aqueous solution in the presence of a strong mineral acid; for example hydrochloric acid, or in a mixture of an organic acid, for example acetic acid, and a mineral acid at a temperature of from 50—100°C, preferably from 60—80°C. The reaction of compounds III and IV is conventional and may be carried out in known manner.

The compounds of formulae II, III IV are either known or may be prepared from known compounds by conventional methods.

The anion $A^{\ominus}$ in compounds of formula I may be a non-chromophoric organic or inorganic anion, for example chloride, bromide, sulphate, bisulphate, methylsulphate, aminosulphate, perchlorate, chlorozincate, tetrafluoroborate, lactate, succinate, tartrate, malate, methansulphonate or benzoate; or may be a complex anion for example of boric, citric, glycollic, diglycollic or adipic acids.

The anion $A^{\ominus}$ may be exchanged for other anions for example with the aid of an ion-exchange resin or by reaction with salts or acids. Such reaction may take place in more than one step, for example through the hydroxide or bicarbonate, or according to French Patent 2,028,725 or 2,028,726.

The compounds of formula I are dyestuffs and are useful for the dyeing of cationically dyeable substrates such as leather, paper and plastics, and particularly for the dyeing or printing of textile substrates containing or consisting of fibres of homopolymers or copolymers of acrylonitrile or asymmetric dicyanoethylene, or of acid-modified polyamides or polyesters. Such polyamides and polyesters are described in Belgian Patent 706 104 and U.S. Patent 3,379,723 respectively.

The compounds may be worked up by conventional means into solid or liquid compositions, for example by granulation or by dissolving in a suitable solvent, optionally in the presence of additives such as stabilisers or solubilising agents such as urea. Such preparations may be obtained for example as described in French Patents 1,572,030 and 1,581,900 or German Patent Publications 2,001,748 and 2,001,816.

Polymers may be dyed for example by the continuous gel-dyeing process, for which liquid compositions of the dyes are particularly suitable. Textile material may be dyed in neutral or acidic aqueous media at temperatures of from 60°—100°C at atmospheric pressure or at temperatures over 100°C under pressure. Alternatively, dyeing may be carried out in organic solvents, for example as described in German Patent Publication 2,437,549.

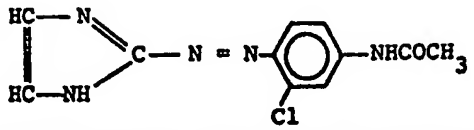
The dyestuffs exhibit good build-up power and give deep, brilliant dyeings having good fastnesses, for example fastness to light, ironing, heat, steam, washing, sweat, pleating, decatizing, dry cleaning and cross-dyeing. The dyestuffs reserve wool, and have notable pH-stability, combination properties, migration, stability to boiling, resistance to hydrolysis, good solubility, and high saturation limits and are scarcely affected by electrolytes.

The compounds of formula I are primarily useful for giving even dyeing of polyacrylonitrile materials of varying exhaust rates. In dyeing such materials, the compounds of formula I particularly those having cation molecular weights below 290, show good migration properties and can be dyed without the use of a retarder. If they are dyed in the presence of a retarder it is advantageous if the retarder also has good migration properties. Slow-, normal-, or fast-exhaust polyacrylonitrile materials are described for example in German Offenlegungsschrift 2,548,009.

The following Examples, in which parts and percentages are by weight, and temperatures are in degrees Centigrade, illustrate the invention.

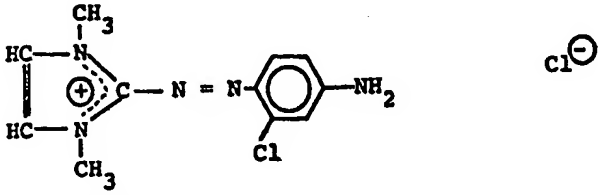
EXAMPLE 1

37 Parts 2-chloro-4-acetylaminoaniline are added to 350 parts water, 100 parts acetic acid and 50 parts 30% hydrochloric acid and diazotised with 60 parts 4N sodium nitrite at 0—5°. After removal of excess nitrous acid with 1.5 parts aminosulphonic acid, the clear diazonium salt solution is dropped into a solution of 13.6 parts imidazole in 100 parts water at 0—5°. During coupling the pH is held at 9—10 by addition of 30% sodium hydroxide solution, and the temperature held below 5° by adding ice. The suspension is stirred for 2 hours, filtered and the residue washed and dried at 50° in vacuo, to give a compound of formula:



This intermediate (27.5 parts) is suspended in 250 parts water containing 2.5 parts sodium carbonate, and the suspension warmed to 40°. Then 63 parts dimethyl sulphate is added all at once, and the mixture stirred for 3 hours at 35—40°, the pH being kept at 7.5—8.5 by addition of 30% NaOH solution, until thin layer chromatography shows no remaining starting material. After addition of 130 parts of 26% brine and 20 parts zinc chloride the dye suspension is stirred, cooled, filtered and washed with 15% brine.

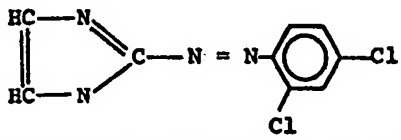
The moist filter cake is finally stirred in 400 parts 6% HCl and heated to 75° for 2 hours. The solution is then brought to pH 6 by addition of 30% NaOH solution and the resulting suspension filtered at 40—50°, washed with 100 parts 10% brine and dried in a vacuum oven at 50—60°, to give the dyestuff of formula:



The product dyes polyacrylonitrile and anionic-modified polyester fibres at fast orange to scarlet-red tones, and show good migration properties on polyacrylonitrile.

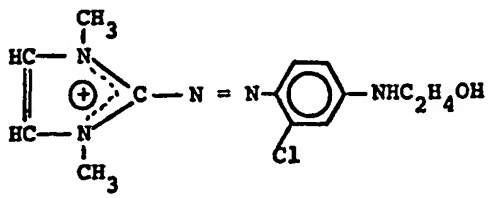
EXAMPLE 2

In manner analogous to Example 1, 2,4-dichloroaniline is coupled to imidazol to give the compound of formula:



48 parts of which are stirred into 500 parts dioxane at 40° and treated with 84 parts magnesium oxide. Dimethyl sulphate (110 parts) is added dropwise over 1 hour, and the mixture is stirred for 1—2 hours, then diluted with 600 parts water at 40°. The yellow solution is treated with 15 parts activated charcoal, clear filtered, evaporated to half of its volume under reduced pressure, clear filtered a second time and treated with 14 parts zinc chloride and 280 parts 26% brine. The yellow suspension is stirred for 2 hours, and the precipitated dyestuff filtered off, washed with a little cold 10% brine and vacuum dried at 50°.

The quaternised product (41.5 parts, 90% pure) is added to a solution of 40 parts ethanolamine and 1.5 parts glacial acetic acid in 500 parts water at 50°, and the mixture stirred for 2 hours, then cooled to room temperature. After clear filtration, the scarlet-red filtrate is brought to pH 5—5.5 with HCl, then 100 parts NaCl are added and the precipitated dyestuff is filtered off after stirring for 4 hours. the red dye may be further purified by solution in 10% acetic acid, extraction with toluene or trichloroethylene, and reprecipitation as the chloride salt. The resulting dyestuff, of formula:



dyes polyacrylonitrile and acid-modified polyester fibres in fast orange to scarlet tones.

EXAMPLES 3—18

In manner analogous to Examples 1 and 2, and using corresponding starting materials, dyestuffs of formula I may be obtained in which R_3 and R_4 are hydrogen and R_1, R_2, R_5 and R_6 are as listed in the following Table.

The anion $A^{\ominus}$ may be any one of those listed above.

Ex. No.	R_1	R_2	R_6	R_5
3	$-CH_3$	$-CH_3$	F	H
4	do.	do.	F	$-CH_3$
5	do.	do.	F	$-C_2H_5$
6	do.	do.	F	$-C_2H_4-OH$
7	do.	do.	F	$-C_3H_6OH$
8	do.	do.	F	$-C_3H_6OCH_3$
9	do.	do.	F	$-C_4H_9$
10	do.	do.	Cl	$-CH_3$
11	do.	do.	Cl	$-C_2H_5$
12	do.	do.	Cl	$-CH_2-CHOH-CH_3$
13	do.	do.	Cl	$-C_3H_6OCH_3$
14	do.	do.	Cl	$-C_4H_9$
15	$-CH_3$	$-CH_3$	Cl	$-C_3H_7$
16	$-C_2H_5$	$-C_2H_5$	Cl	H
17	$-CH_3$	$-CH_3$	Cl	$-CH_2-CH(CH_3)_2$
18	do.	do.	F	do.

The dyestuffs of Examples 3 and 16 dye polyacrylonitrile in orange tones, those of the remaining Examples in scarlet tones.

APPLICATION EXAMPLE A

Polyacrylonitrile fibres are added to an aqueous dyebath at 60° containing 0.125 g/l glacial acetic acid, 0.375 g/l sodium acetate and 0.15 g/l of the dyestuff of Examples 1 (or a corresponding quantity of solid or liquid preparation of this dyestuff), the liquor-to-goods ratio being 80:1. The dyebath is brought to the boil over 20—30 min., and kept at the boil for 90 min. The substrate is rinsed and dried to give an orange dyeing with good fastness properties.

APPLICATION EXAMPLE B

Acid-modified polyester fibres are added to an aqueous dyebath at 20°, containing 3 g/l sodium sulphate, 2 g/l ammonium sulphate and 2.5 g/l of a nonionic carrier, the liquor-to-goods ratio being 40:1. The pH is regulated to 5.5 by addition of formic acid. The bath is heated to 60°, and 0.15 g/l of the dyestuff of Example 1 (or a corresponding amount of a solid or liquid preparation thereof) is added. The bath is heated to boiling point over 30 minutes, and held at the boil for 60 min. After rinsing and drying, an orange dyeing with good fastness properties is obtained.

APPLICATION EXAMPLE C

Acid-modified polyester fibres are added to an aqueous dyebath at 20°C containing 6 g/l sodium sulphate, 2 g/l ammonium sulphate and 0.15 g of the dyestuff of Example 1 (or a corresponding amount of a solid or liquid preparation thereof). The liquor-to-goods ratio is 30:1. The pH is regulated to 5.5 with formic acid, and the bath is heated in a closed vessel to 110—120° over 45 minutes, and held at that temperature, with shaking, for 60 minutes. After rinsing and drying, an orange dyeing with good fastness properties is obtained.

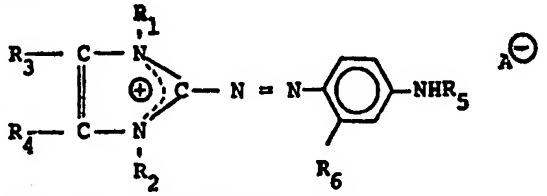
APPLICATION EXAMPLE D

Acid-modified polyamine fibres are added to an aqueous dyebath at 20°, containing 3.6 g/l potassium dihydrogen phosphate, 0.7 g/l disodium hydrogen phosphate, 1 g/l of an auxiliary consisting of the reaction product of a phenol with excess ethylene oxide, and 0.15 g/l of the dyestuff of Example 1 (or a corresponding amount of a solid or liquid preparation thereof). The liquor-to-goods ratio is 80:1. The bath is heated to the boil over 30 minutes and kept at the boil for 60 minutes. After rinsing and drying an orange dyeing with good fastness properties is obtained.

The dyestuffs of the remaining Examples may be applied in the same way.

CLAIMS

1. A compound of formula I



I

in which R_1 and R_2 are independently unsubstituted C_{1-4}alkyl,
R_3 and R_4 are independently hydrogen or unsubstituted C_{1-4}alkyl,
R_5 is hydrogen, unsubstituted C_{1-4}alkyl or C_{2-4}alkyl mono-substituted by OH or C_{1-4}alkoxy,
R_6 is halogen and
$A^{\ominus}$ is an anoin.

2. A compound as claimed in Claim 1 in which R_1 and R_2 are independently methyl or ethyl.

3. A compound as claimed in Claim 2 in which R_1 and R_2 are both methyl.

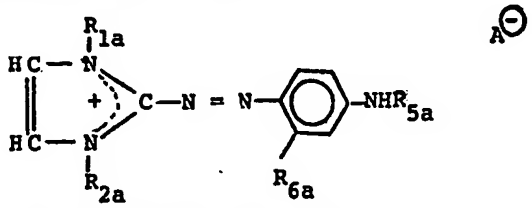
4. A compound as claimed in any one of the preceding claims in which R_3 and R_4 are both hydrogen.

5. A compound as claimed in any one of the preceding claims in which R_5 is hydrogen, methyl, ethyl, 2-hydroxymethyl, 2-hydroxypropyl or 3 methoxypropyl.

6. A compound as claimed in Claim 5 in which R_5 is hydrogen or methyl.

7. A compound as claimed in any one of the preceding claims in which R_6 is fluorine or chlorine.

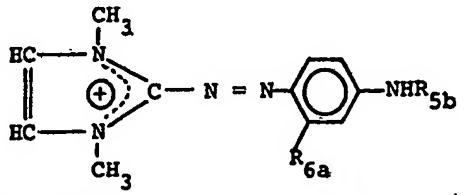
8. A compound as claimed in Claim 1 of formula Ia



Ia

in which R_{1a} and R_{2a} are independently methyl or ethyl,
R_{5a} is hydrogen, methyl, ethyl, 2-hydroxymethyl, 2-hydroxypropyl or 3-methoxypropyl,
R_{6a} is fluorine or chlorine, and $A^{\ominus}$ is an anion.

9. A compound as claimed in Claim 8 of formula Ib

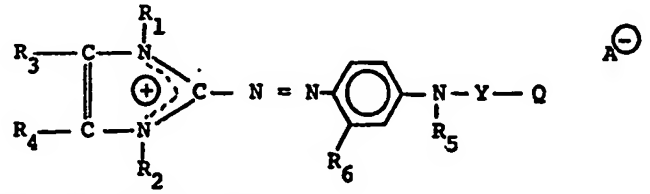


Ib

in which R_{5b} is hydrogen or methyl,
R_{6a} is as defined in Claim 8, and $A^{\ominus}$ is an anion.

10. A compound as claimed in Claim 9 of formula Ib, stated in Claim 9, in which R_{5b} is hydrogen and R_{6b} is chlorine.

11. A process for the preparation of a compound of formula I, stated in Claim 1, characterised by either a) treating a compound of formula II



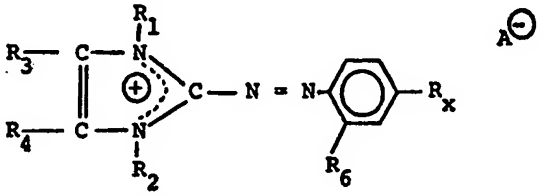
II

in which R_{1-6} and $A^{\ominus}$ are as defined in Claim 1,

Y is —CO— or —SO_2

and Q is C_{1-4} alkyl

with an acid HA in which A is a group capable of forming the anion $A^{\ominus}$, or
(b) by reacting a compound of formula III



III

in which R_1, R_2, R_3, R_4, R_6 and $A^{\ominus}$ are as defined in Claim 1 and R_x is an anionic leaving group, with a compound of formula IV

$$R_5\text{——}NH_2 \qquad \text{IV}$$

in which R_5 is as defined in Claim 1.

12. A compound of formula I, stated in Claim 1, whenever prepared by a process as claimed in Claim 11.

13. A compound of formula I, as described in any one of Examples 2—18.

14. A process for the dyeing or printing of basic dyeable substrates comprising application of a dyestuff as claimed in Claim 1.

15. Basic-dyeable substrates whenever dyed by the process of Claim 14.

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